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(54) Polymeric piezoelectric material

(57) A polymeric piezoelectric material is obtained by heat-electretizing a molded product of a polyester containing an aromatic hydroxycarboxylic acid residue and exhibiting anisotropy in the molten state and/or a polyester containing partly in the same molecular chain a polyester exhibiting anisotropy in the molten state. The material can be used at above 150°C in a variety of applications, eg. pressure sensitive element, movable element, acoustic transducer, medical transducer, infrared and radiation sensor.

SPECIFICATION

Polymeric piezoelectric material

- 5 The present invention relates to a polymeric piezoelectric material obtained by heat-electretizing the molded product of a polyester which contains an aromatic hydroxycarboxylic acid residue and exhibits the anisotropism in the molten state. 5

It is known to persons skilled in the art that a polymeric ferroelectric material can be used as a piezoelectric material or pyroelectric material when it is heat-electretized to give an electret element. Known examples of

- 10 such polymeric piezoelectric material include polyvinylidene fluoride, polytrifluoroethylene, and polyvinylidene cyanide-vinyl acetate copolymer. 10

These polymeric piezoelectric materials are soft and can be easily made into film of large area. Because of the good moldability characteristic of polymers the inorganic piezoelectric materials do not possess, they are expected to find a wide range of applications.

- 15 However, these polymeric piezoelectric materials are limited in temperature at which they are used. This is because the piezoelectric property is derived from the high order structure of the polymer. In other words, the direction of the dipole moment in the molecular chain is changed and frozen when the polymer is heat-electretized. Therefore, they cannot be used at temperatures higher than about 140 to 160°C. 15

In view of the above-mentioned problems, the present inventors carried out extensive studies to develop a

- 20 new polymeric piezoelectric material which can be used at higher temperatures and can be easily heat-electretized. In their studies, the present inventors paid their attention to the fact that a polymer that exhibits the anisotropism in the molten state, or a liquid crystal polymer, is easily mobile for polarization orientation. It was found that the one containing an aromatic hydroxycarboxylic acid residue in the molecular chain has the anisotropism of dipole. This finding led to the present invention. 20

- 25 Accordingly, the present invention relates to a polymeric piezoelectric material which is obtained by heat-electretizing a molded product of a polyester containing an aromatic hydroxycarboxylic acid residue which exhibits the anisotropism in the molten state and/or a polyester containing partly in the same molecular chain a polyester which exhibits the anisotropism in the molten state. 25

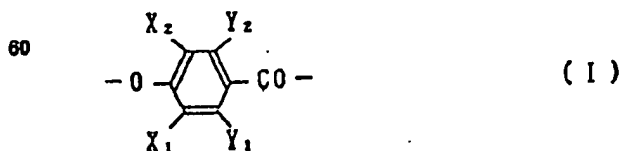
The polyester used in this invention is a polymer composition which exhibits the optical anisotropism in the molten state and is capable of thermoplastic melt-processing. It generally falls under the category of thermotropic liquid crystal polymer. 30

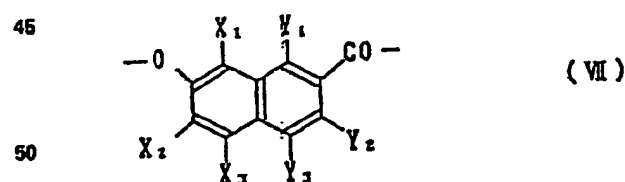
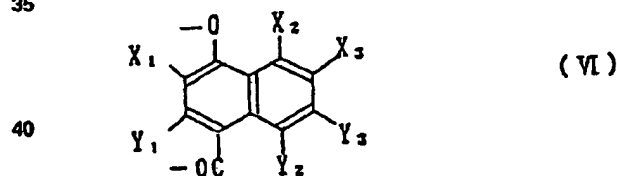
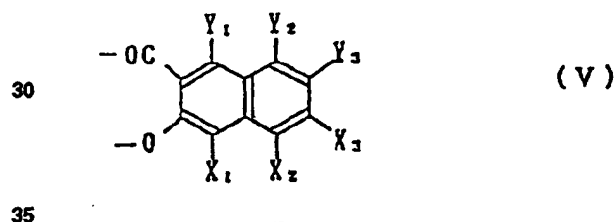
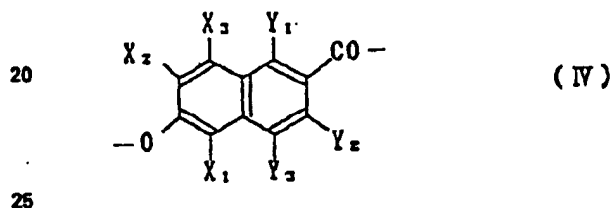
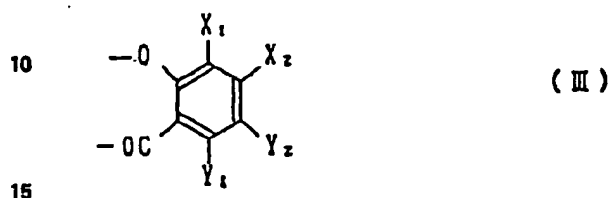
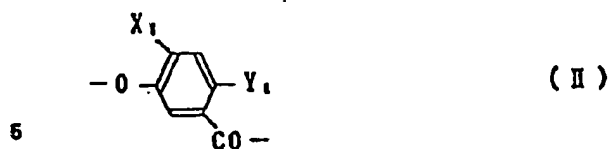
The polymer which forms the anisotropic molten phase has the properties of permitting the polymer molecular chains to assume regular parallel arrangement in the molten state. The state in which molecules are arranged in such a manner is referred to as the liquid crystal state. The polymer like this is usually produced from a monomer which has a thin, long, and flat configuration, has a high rigidity along the long axis of the molecule, and has a plurality of chain extension linkages which are coaxial or parallel with one another. 35

The properties of the anisotropic molten phase can be determined by an ordinary polarization test using crossed nicols. More particularly, the properties can be determined with a Leitz polarizing microscope of 40 magnifications by observing a sample placed on a Leitz hot stage in a nitrogen atmosphere. The polymer is optically anisotropic. Namely, it transmits a light when it is placed between the crossed nicols. When the sample is optically anisotropic, the polarized light can be transmitted through it even in a still state. 40

The resin molded product of this invention is characterized in that the polyester which exhibits the anisotropism in the molten state is one which contains an aromatic hydroxycarboxylic acid residue and aromatic substituted derivative residue thereof. The hydroxy group and carboxylic acid group should preferably be substituted directly on the aromatic ring, and the hydroxyl group and carboxylic acid group may be on the same aromatic ring or different aromatic rings. In either cases, they should be in the same molecule of the aromatic cyclic compound. The aromatic hydroxycarboxylic acid resin should preferably be a compound composed of one or more kinds selected from the hydroxybenzoic acid residue, 45

- 50 hydroxynaphthoic acid residue, and their aromatic substituted derivative residue. The aromatic substituted derivative residue should have the substituent group selected from functional group which imparts the anisotropism to the intramolecular dipole moment of the hydroxycarboxylic acid compound and is at the substitution position to impart such anisotropism. In addition, the substituent group of the aromatic substituted derivative residue is one which imparts the anisotropism to the dipole moment in the direction of the line connecting the carbon atoms on the aromatic ring to which the hydroxyl group and carboxylic acid group are connected, and is at the substitution position to impart such anisotropism. Preferred examples are those represented by the following formulas (I) to (VII). 55





(wherein the group consisting of X_1 , X_2 , and X_3 and the group consisting of Y_1 , Y_2 , and Y_3 are separated by a line which intersects at right angles a line connecting the carbon atoms on the aromatic ring to which the hydroxyl group and carboxylic acid group are connected, at the center thereof; each of said groups is one or more kinds selected from substituent groups which differ from one another in dipole moment; the same group does not contain those which differ from one another in the direction of dipole moment; and the unsubstituted position in each group represents a hydrogen atom.)

The substituent group is selected from cyano group, nitro group, aldehyde group, carboxylic acid ester, carboxylic acid group, hydroxyl group, hydrogen, halogen compound, amino group, imino group, azo group, alkoxy group, alkyl group, phenyl group, acyl group, sulfoxy group, and sulfide group. Preferably, it is selected from hydrogen, cyano group, nitro group, acetoxy group, chlorine, bromine, phenyl group, alkyl group, methoxy group, amino group, and alkyl-substituted amino group.

The above-mentioned polyester which exhibits the anisotropism in the molten state may be a

homopolymer or a block or graft copolymer. In the latter case, the segments of the polyester are copolymerized in the other polyester which may not be capable of polarization orientation. The other polyester is one or more kinds selected from aromatic polyester, polycarbonate, polyethersulfone, polyacrylate, and polyalkylene terephthalate.

- 5 The polymer which exhibits the anisotropism in the molten state may be contained in the other thermoplastic polymer. It may be dispersed in the miscible form or immiscible form. Those which are uniformly dispersible are preferable, and their examples include aromatic polyester, polycarbonate, polyether sulfone, polyacrylate, and polyalkylene terephthalate.

The polyester which exhibits the anisotropism in the molten state may be produced by a variety of ester-forming processes.

- 10 The monomer compounds can be reacted by melt acidolysis in the absence of any heat exchange fluid. In this process, the monomers are heated to form a melt of reactants. As the reaction proceeds, the solid polymer particles begin to suspend in the melt. In the final stage of the condensation reaction, the reaction system may be evacuated to facilitate the removal of volatile by-products such as acetic acid and water.

- 15 A slurry polymerization process may also be employed in the preparation of fully aromatic polyesters suitable for use in the present invention. In this process, the solid product is obtained in the form of suspension in a heat exchange medium.

In either of said melt acidolysis and slurry polymerization processes, the organic monomeric reactants from which the fully aromatic polyesters can be derived may be employed in the reaction in a modified form obtained by esterifying the hydroxyl group of the monomer at ambient temperature (i.e., in the form of their lower acyl esters). The lower acyl groups have preferably about 2 to 4 carbon atoms. Preferably, acetate esters of the organic monomeric reactants are employed in the reaction. Also, the modified form (i.e., phenol ester) formed by esterifying the carboxylic acid group may be used for the reaction.

- 20 Typical examples of the catalysts that can be used in both of the melt acidolysis and slurry processes include dialkyltin oxides (such as dibutyltin oxide), diaryltin oxides, titanium dioxide, antimony trioxide, alkoxytitanium silicates, titanium alkoxides, alkali metal and alkaline earth metal salts of carboxylic acids (such as zinc acetate), Lewis acids (such as BF_3), and hydrogen halides and other gaseous acids (e.g., HCl). The catalyst is generally used in an amount of about 0.001 to 1 wt%, particularly about 0.01 to 0.2 wt%, based on the monomer.

- 30 The aromatic polymers suitable for use in the present invention are substantially insoluble in ordinary solvents and, therefore, they are unsuitable for use in a solution processing. However, these polymers can be processed easily by the ordinary melt processing. Particularly preferred aromatic polymers are soluble in pentafluorophenol to some extent.

The aromatic polyester which is preferably used in the present invention have a weight-average molecular weight of about 1,000 to 200,000, preferably about 2,000 to 50,000, particularly about 3,000 to 25,000.

- 35 The molecular weight may be determined by gel permeation chromatography or other standard methods which need no polymer solution, such as a method in which terminal groups are determined by infrared spectroscopy using a compression-molded film sample. The molecular weight may also be determined by the light-scattering method using a solution of pentafluorophenol.

- 40 The above-mentioned aromatic polyester has an inherent viscosity (I.V.) of at least about 0.5 dl/g, for example, about 0.5 to 10.0 dl/g as measured in a 0.1 wt% solution in pentafluorophenol at 60°C.

The polyester which exhibits the anisotropism in the molten state may contain another ferroelectric substance. Such ferroelectric compound enhances the properties of the polyester used as a ferroelectric material. The ferroelectric compound may be inorganic compounds, organic compounds, or polymeric compounds.

- 45 Examples of the inorganic compounds include quartz, lead zirconate titanate, potassium hydrogen phosphate, barium titanate, lead titanate, lead niobate, lithium niobate, lithium tantalate, strontium barium niobate, $\text{Pb}(\text{B}_1\text{B}_2)\text{O}_3$, and $\text{PbTiO}_3\text{-PbZrO}_3\text{-Pb}(\text{B}_1\text{B}_2)\text{O}_3$ (where B_1 represents Mg, Co, Ni, Mn, or Zn; and B_2 represents Nb, Ta, Sb, or W).

- 50 Examples of the organic compounds include low molecular liquid crystal compounds, Rochelle salt, and triglycin sulfate. Explanations on low-molecular liquid crystal compounds will be found in "Ekisho no Saishin Gijutsu" (Latest Technology of Liquid Crystals) by Matsumoto and Tsunoda (Kogyo Chosakai) and "Handbook of Liquid Crystals" by K. Kelker and R. Hatz (Weinheim, 1980).

Examples of the polymeric compound include polymers and copolymers of vinylidene fluoride, trifluoroethylene, vinylidene cyanide, and chloroacrylonitrile.

- 55 The polyester obtained in this invention is usually heat-electretized when it is formed into sheet or film. After the heat-electretizing, it may be used in the form of powder having polarization orientation. This powder may also be dispersed into a thermosetting or thermoplastic resin.

Examples of the thermosetting resin include phenolic resin, epoxy resin, melamine resin, urea resin, unsaturated polyester resin, and alkyd resin.

- 60 Examples of the thermoplastic resin include polyethylene, polypropylene, polybutylene, polybutadiene, polyisoprene, polyvinyl acetate, polyvinyl chloride, polyvinylidene chloride, polystyrene, acrylic resin, ABS resin, AS resin, BS resin, polyurethane, silicone resin, fluoroplastic, cyan resin, polyacetal, polycarbonate, polyethylene terephthalate, polybutylene terephthalate, aromatic polyester, polyamide, polyacrylonitrile, polyvinyl alcohol, polyvinyl ether, polyetherimide, polyamideimide, polyetherimide, polyetherketone,

polyethersulfone, polysulfone, polyphenylene sulfide, and polyphenylene oxide.

Preferred ones are aromatic polyester, polycarbonate, polyether sulfone, polyacrylate, polyalkylene terephthalate, and polymers and copolymers derived from vinylidene fluoride, trifluoroethylene, vinylidene cyanide, and chloroacrylonitrile.

- 5 In another usage, the composite material containing a heat-electretized powder may be further heat-electretized. 5

The heat-electretizing can be carried out by the method known to persons skilled in the art. Both sides of the sheet or film of the polyester of this invention are treated for electric conduction, and a voltage is applied to the sheet or film with heating. The voltage application may be performed continuously or intermittently (in pulse). The intermittent application in pulse is preferred for the ease of polarization orientation. The object is 10 achieved with minimum heating sufficient to impart kinetic energy that causes the polarization inversion. For complete polarization inversion, the heating temperature should be higher than the melting point of the polyester. At such a temperature the polarization orientation takes place very quickly because of the properties of liquid crystal the polyester originally possesses. Where the polarized anisotropic strain is 15 required, it is possible to control the temperature and the intensity of electric field. 15

The polyester and composite product thereof obtained in this invention may be incorporated with a variety of additives by the method known to persons skilled in the art. The additives include plasticizer, antioxidant, UV light absorber, antistatic agent, flame retardant, dye and pigment, surface treatment therefor, and reinforcing fiber and inorganic filler.

- 20 The present invention provides a polymeric piezoelectric material which is obtained by heat-electretizing a molded product of a polyester which contains an aromatic hydroxycarboxylic acid residue and exhibits the anisotropism in the molten state and/or a polyester containing partly in the same molecular chain a polyester which exhibits the anisotropism in the molten state. The polymeric piezoelectric material has several features. It has extremely high heat resistance. The molecules are extremely mobile in the molten state 25 because the molecular chain is rigid. It is quickly responsive to the heat-electretizing. Therefore, the polymeric piezoelectric material of this invention finds a large variety of applications. It can be used in a hot environment above 150°C in which the ordinary ferroelectric polymeric materials cannot be used. It can be used as a heat-resistant piezoelectric material such as a pressure-sensitive element, movable element, acoustic transducer, and a medical transducer. It can also be used as a pyroelectric material as an infrared 30 sensor and radiation sensor. Detailed explanations on these application will be found in "Fine Electronics and High-functional Materials", edited by Higaki (CMC Co., Ltd., June 1983), P. 168. 30

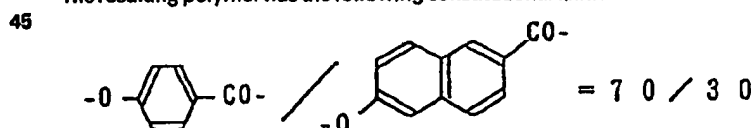
The invention is now described in more detail with reference to the following examples, which should not be construed as limiting the scope of the invention.

35 Example 1 35

- 1261 parts by weight of 4-acetoxybenzoic acid and 691 parts by weight of 6-acetoxy-2-naphthoic acid were placed in a reactor provided with a stirrer, a nitrogen inlet tube, and a distillation tube. The mixture was heated to 250°C under a nitrogen stream and stirred vigorously at that temperature for 3 h and then at 280°C for 2 h while acetic acid was distilled off from the reactor. The temperature was elevated at 320°C and the 40 feeding of nitrogen was stopped. The pressure in the reactor was reduced gradually to 0.1 mmHg after 20 min. The mixture was stirred at that temperature under that pressure for 1 h. 40

The resulting polymer had an intrinsic viscosity of 5.4 as determined in pentafluorophenol at a concentration of 0.1 wt% at 60°C.

The resulting polymer has the following constitutional units.



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- The resulting polymer was made into a 20-μm thick film by using a T-die extruder. The extruder and T-die were set at 300°C and 290°C respectively. The film was stretched at a draw ratio of 1/10. Both sides of the film were coated with silver by vapour deposition. The film was heated at 260°C and subjected to the application 55 of DC voltage (100 kV/cm) for 60 minutes. After that, the film was cooled rapidly. The resulting test piece had a piezoelectric constant d_{31} of 8.5×10^{-6} CGSesu and a pyroelectric constant of 5.7×10^{-10} C/cm²·K. Ad_{31} measured in the same manner at 180°C was 10×10^{-6} CGSesu. 55

Example 2

- 60 138.2 parts by weight of polyethylene terephthalate (having an intrinsic viscosity of 0.36) was added to 162 parts by weight of polyester (having an intrinsic viscosity of 0.77) preliminarily polymerized at 260°C for 3 hours in the same manner as in Example 1. The reaction was continued in the same reactor at 280°C for 4 hours with vigorous agitation. The reaction temperature was raised to 320°C and the feeding of nitrogen was stopped. The reactor was evacuated to 0.1 mmHg after 15 minutes. Stirring was continued for 1 hour at 65 this temperature and pressure. 65

The resulting polymer had an intrinsic viscosity of 2.9 as determined in pentafluorophenol at a concentration of 0.1 wt% at 60°C.

The resulting polymer was found to be composed of 40 mol% of polyethylene terephthalate and 60 mol% of hydroxybenzoic acid and hydroxynaphthoic acid.

- 5 A test piece was prepared in the same manner as in Example 1, and it was heated at 200°C and subjected to the application of DC voltage (100 kV/cm) for 60 minutes. The resulting test piece had a piezoelectric constant d_{31} of 9.1×10^{-8} CGSesu and a pyroelectric constant of 6.2×10^{-10} C/cm²K. A d_{31} measured in the same manner at 160°C was 12×10^{-8} CGSesu.

10 Example 3

900 parts by weight of 4-acetoxybenzoic acid, 431 parts by weight of 4-acetoxy-3-chlorobenzoic acid, and 690 parts by weight of 6-acetoxy-2-naphthoic acid were placed in a reactor provided with a stirrer, a nitrogen inlet tube, and a distillation tube. The mixture was heated to 250°C under nitrogen stream and stirred vigorously at that temperature for 3 h and then at 280°C for 2 h while acetic acid was distilled off from the reactor. The temperature was elevated to 320°C and the feeding of nitrogen was stopped. The pressure in the reactor was reduced gradually to 0.1 mmHg after 20 min. The mixture was stirred at that temperature under that pressure for 1 h.

The resulting polymer had an intrinsic viscosity of 5.0 as determined in pentafluorophenol at a concentration of 0.1 wt% at 60°C.

- 20 A test piece was prepared in the same manner as in Example 1, and it was heated at 220°C and subjected to the application of DC voltage (100 kV/cm) for 60 minutes. The resulting test piece had a piezoelectric constant d_{31} of 8.8×10^{-8} CGSesu and a pyroelectric constant of 5.9×10^{-10} C/cm²K. A d_{31} measured in the same manner at 160°C was 12×10^{-8} CGSesu.

25 Comparative Example 1

166 parts by weight of terephthalic acid, 166 parts by weight of isophthalic acid, and 250 parts by weight of diacetoxyethylhydroquinone were placed in a reactor provided with a stirrer, a nitrogen inlet tube, and a distillation tube. The mixture was heated to 260°C under a nitrogen stream and stirred vigorously at that temperature for 2.5 h and then at 280°C for 3 h while acetic acid was distilled off from the reactor. The temperature was elevated at 320°C and the feeding of nitrogen was stopped. The pressure in the reactor was reduced gradually to 0.1 mmHg after 15 min. The mixture was stirred at that temperature under that pressure for 1 h.

The resulting polymer had an intrinsic viscosity of 0.87 as determined in a 1:1 mixed solvent of tetrachloroethane and phenol at a concentration of 0.5 wt%.

- 35 The resulting polymer was heat-electretized in the same manner as in Example 3. The piezoelectric constant d_{31} was 9.2×10^{-8} CGSesu.

Example 4

The polymer obtained in Example 1 was slowly and uniformly incorporated with ceramics powder of lead zirconate-titanate ($\text{PbZrO}_3\text{-PbTiO}_3$) while heating at 280°C with hot rolls. The amount of the ceramics powder was 30 vol% in the resulting composite material. The resulting composite was made into a 50- μm thick film by using a hot press. The resulting film was made into a test piece in the same manner as in Example 1. The test pieces at 220°C was subjected to the application of DC electric field (200 kV/cm) for 60 minutes. The piezoelectric constant d_{31} was 2.6×10^{-7} CGSesu.

45 Example 5

The polymer obtained in Example 2 was made into a 50- μm thick film in the same manner as in Example 4. The hot rolls were heated to 220°C. The test pieces at 220°C was subjected to the application of DC electric field (200 kV/cm) for 60 minutes. The piezoelectric constant d_{31} was 2.7×10^{-7} CGSesu.

50 Example 6

The polymer obtained in Example 1 was heated to 280°C using a hot press. While being held between copper plates, the polymer at 280°C was subjected to the application of DC electric field (100 kV/cm) for 60 minutes, followed by rapid cooling. The resulting film underwent cryogenic grinding at -60°C. There was obtained needle powder. The powder was uniformly incorporated into polyacetal ("Duracon M-90", a product of Polyplastics Co., Ltd.) using hot rolls at 180°C. The amount of the powder was 40 vol% based on the resulting composite. The resulting composite was made into a 50- μm thick film using a hot press. The film at 100°C was subjected to the application of DC electric field (200 kV/cm) for 60 minutes in the same manner as in Example 1. The piezoelectric constant d_{31} was 2.2×10^{-8} CGSesu. Incidentally, the piezoelectric constant of the polyacetal measured in the same manner was 7.7×10^{-10} CGSesu.

Example 7

The electretized needle powder obtained in Example 6 was incorporated with polyvinylidene fluoride resin (KF-1100 made by Kureha Chemical Co., Ltd.) using hot rolls in the same manner as in Example 6. The amount of the powder was 50 vol% based on the resulting composite. The test piece at 100°C was subjected to the

application of DC electric field (200 kV/cm) for 60 minutes. The piezoelectric constant d_{31} was 1.5×10^{-7} CGSesu. Incidentally, the piezoelectric constant of the polyvinylidene fluoride alone measured in the same manner was 1.0×10^{-7} CGSesu.

5 Example 8

The polymer obtained in Example 1 underwent cryogenic grinding at -60°C . There was obtained needle powder. The powder was uniformly incorporated into polybutylene terephthalate ("Duranex 2002", a product of Polyplastics Co., Ltd.) using hot rolls at 230°C . The amount of the powder was 50 vol% based on the resulting composite. The resulting composite was made into a $50\text{-}\mu\text{m}$ thick test piece using a hot press. The test piece at 200°C was subjected to the application of DC electric field (200 kV/cm) for 60 minutes in the same manner as in Example 1. The piezoelectric constant d_{31} was 4.0×10^{-8} CGSesu. Incidentally, the piezoelectric constant of the polybutylene terephthalate measured in the same manner was 8.0×10^{-10} CGSesu.

Example 9

The polymer obtained in Example 2 was made into needle powder in the same manner as in Example 8, and the powder was made into a test piece which was subsequently electretized. The piezoelectric constant d_{31} was 3.8×10^{-8} CGSesu.

CLAIMS

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1. A polymer piezoelectric material which is obtained by heat-electretizing a molded product of a polyester containing aromatic hydroxycarboxylic acid residue which exhibits the anisotropism in the molten state and/or a polyester containing partly in the same molecular chain a polyester which exhibits the anisotropism in the molten state.

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2. A polymeric piezoelectric material as set forth in Claim 1, wherein the aromatic hydroxycarboxylic acid residue is one or more kinds of compounds selected from hydroxybenzoic acid residue, hydroxynaphthoic acid residue, and aromatic substituted derivative residues thereof.

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3. A polymeric piezoelectric material as set forth in Claim 1, wherein the polyester containing an aromatic hydroxycarboxylic acid resin and also containing partly in the same molecular chain a polyester which exhibits the anisotropism in the molten state is a copolymer composed of a polyester which exhibits the anisotropism in the molten state and one or more kinds selected from other aromatic polyesters, polycarbonate, polyether sulfone, polyacrylate, and polyalkylene terephthalate.

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4. A polymeric piezoelectric material as set forth in Claim 1, wherein the polyester containing an aromatic hydroxycarboxylic acid residue which exhibits the anisotropism in the molten state and/or the polyester containing partly in the same molecular chain a polyester which exhibits the anisotropism in the molten state is contained in other thermoplastic polymer.

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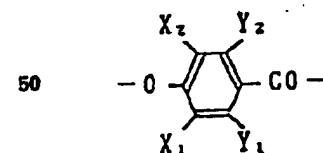
5. A polymeric piezoelectric material as set forth in Claim 2, wherein the substituent group of the aromatic substituted derivative residue is one which imparts the anisotropism to the intramolecular dipole moment of the hydroxycarboxylic acid compound and is at the substitution position to impart such anisotropism.

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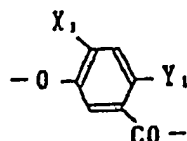
6. A polymeric piezoelectric material as set forth in Claim 2, wherein the substituent group of the aromatic substituted derivative residue is one which imparts the anisotropism to the dipole moment in the direction of the line connecting the carbon atoms on the aromatic ring to which the hydroxyl group and carboxylic acid group are connected, and is at the substitution position to impart such anisotropism.

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7. A polymeric piezoelectric material as set forth in Claim 2, wherein the aromatic hydroxycarboxylic acid residue is composed of one or more kinds selected from the following formulas (I) to (VII).

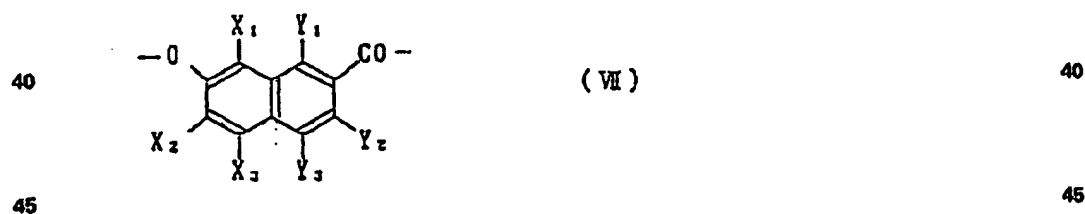
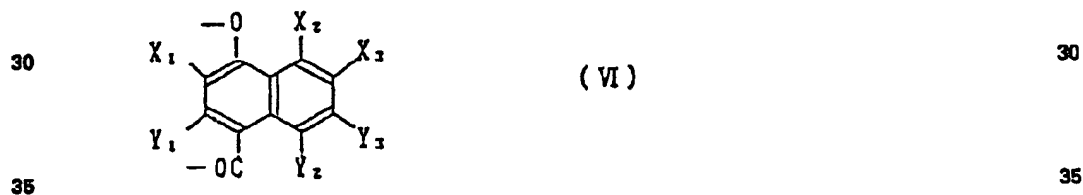
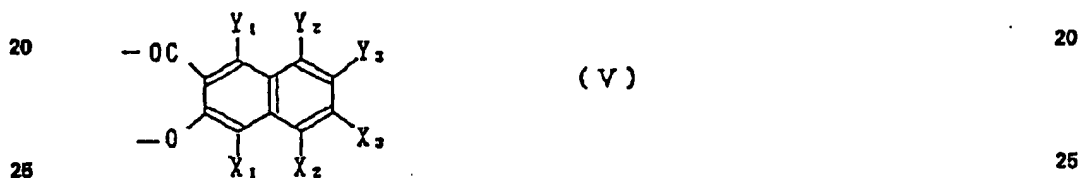
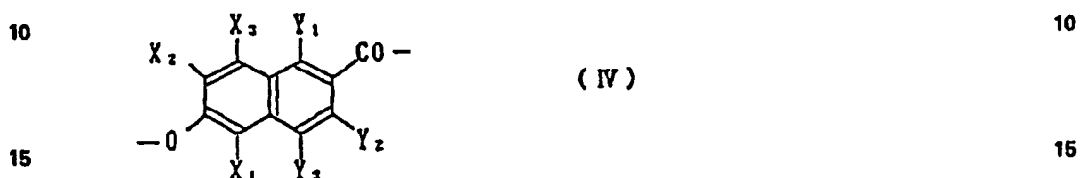
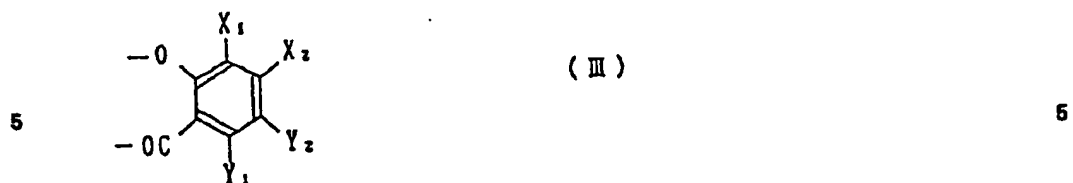


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(wherein the group consisting of X_1 , X_2 , and X_3 and the group consisting of Y_1 , Y_2 , and Y_3 are separated by a line which intersects at right angles a line connecting the carbon atoms on the aromatic ring to which the hydroxyl group and carboxylic acid group are connected, at the center thereof; each of said groups is one or more kinds selected from substituent groups which differ from one another in dipole moment; the same group does not contain those which differ from one another in the direction of dipole moment; and the unsubstituted position in each group represents a hydrogen atom.)

8. A polymeric piezoelectric material as set forth in any of Claims 5 to 7, wherein the substituent group is one or more kinds selected from cyano group, nitro group, aldehyde group, carboxylic acid ester, carboxylic acid group, hydroxyl group, hydrogen, halogen compound, amino group, imino group, azo group, alkoxy group, alkyl group, phenyl group, acyl group, sulfoxy group, and sulfide group.

9. A polymeric piezoelectric material as set forth in any of Claims 5 to 7, wherein the substituent group is one or more kinds selected from hydrogen, cyano group, nitro group, acetoxy group, chlorine, bromine, phenyl group, alkyl group, methoxy group, amino group, and alkyl-substituted amino group.

10. A polymeric piezoelectric material as set forth in Claim 1, wherein the polyester which exhibits the anisotropism in the molten state is one which has a molecular weight of 2,000 to 50,000.

11. A polymeric piezoelectric material as set forth in Claim 1, wherein the molded product (to be heat-electretized) of the polyester which contains an aromatic hydroxycarboxylic acid residue and exhibits the anisotropism in the molten state and/or a polyester containing party in the same molecular chain a polyester which exhibits the anisotropism in the molten state, is one which contains a ferroelectric

- compound.
12. A polymeric piezoelectric material as set forth in Claim 11, wherein the ferroelectric compound is an organic compound.
13. A polymeric piezoelectric material as set forth in Claim 11, wherein the ferroelectric compounds is an inorganic compound. 5
14. A polymeric piezoelectric material as set forth in Claim 13, wherein the inorganic compound is one or more compounds selected from quartz, lead zirconate titanate, potassium hydrogen phosphate, barium titanate, lead titanate, lead niobate, lithium niobate, lithium tantalate, strontium barium niobate, $\text{Pb}(\text{B}_1\text{B}_2)\text{O}_3$, and $\text{PbTiO}_3\text{-PbZrO}_3\text{-Pb}(\text{B}_1\text{B}_2)$ (where B_1 represents Mg, Co, Ni, Mn, or Zn; and B_2 represents Nb, Ta, Sb, or W). 10
15. A polymeric piezoelectric material as set forth in Claim 12, wherein the organic compound is Rochelle salt or triglycin sulfate.
16. A polymeric piezoelectric material as set forth in Claim 12, wherein the organic compound is a polymeric ferroelectric material.
17. A polymeric piezoelectric material as set forth in Claim 12, wherein the organic compound is a low-molecular ferroelectric liquid crystal compound. 15
18. A polymeric piezoelectric material as set forth in Claim 16, wherein the polymeric ferroelectric material is one or more kinds selected from vinylidene fluoride, trifluoroethylene, vinylidene cyanide, and chloroacrylonitrile.
19. A polymeric piezoelectric material as set forth in Claim 1, which is in the form of sheet or film.
20. A polymeric piezoelectric material as set forth in Claim 1, which is in the form of powder or fiber. 20
21. A polymeric piezoelectric material as set forth in Claim 19, wherein both sides of the filmy polymeric piezoelectric material are coated with electroconductive film.
22. A polymeric piezoelectric material as set forth in Claim 1, wherein the molded product is heat-electretized by the application of direct current or both direct current and alternate current.
25. A polymeric piezoelectric material as set forth in Claim 1, wherein the heat-electretized polymeric piezoelectric material is in the form of fiber. 25
24. A polymeric piezoelectric material as set forth in Claim 1, wherein the heat-electretized polymeric piezoelectric material is in the form of powder and/or short fiber.
25. A polymeric piezoelectric material as set forth in Claim 24, wherein the heat-electretized polymeric piezoelectric material in the form of powder and/or short fiber is dispersed in other resin. 30
30. A polymeric piezoelectric material as set forth in Claim 24, wherein the heat-electretized polymeric piezoelectric material is dispersed in a thermosetting resin.
27. A polymeric piezoelectric material as set forth in Claim 24, wherein the heat-electretized polymeric piezoelectric material is dispersed in thermoplastic resin.
35. A polymeric piezoelectric material as set forth in Claim 27, wherein the thermoplastic resin is one which has a lower melting point than the resin to be heat-electretized. 35
29. A polymeric piezoelectric material as set forth in Claim 27, wherein the thermoplastic resin is one or more kinds selected from polyacetal, polybutylene terephthalate, polyethylene terephthalate, vinylidene fluoride, trifluoroethylene, vinylidene cyanide, and chloroacrylonitrile.
40. A polymeric piezoelectric material as set forth in Claim 25, wherein the resin composition in which the heat-electretized resin is dispersed is further heat-electretized. 40